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**ISOLATION OF FISSION FRAGMENT RADIOACTIVE
ELEMENTS BY EXTRACTION**

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During the period elapsed since the Second Geneva Conference long-lived radioactive fission products, such as Sr^{90} , Pm^{147} , Ce^{144} , Eu^{155} have been increasingly needed. As a result of this, the necessity of creating very simple technological schemes for separating radioactive fission fragment elements grew sharply.

At present, when great quantities of radioactive isotopes are separated an increasingly greater part is played by extraction methods.

Only ten years ago the extraction essentially by organic solvents found application only for separating uranium and plutonium from fission fragment elements and for the separation of the former. In some cases the application of organic solvents was recommended only for separating cerium (IV). But already at the Second Geneva Conference the combined extraction-deposition scheme for separating radioactive fragment elements was reported by the USSR. A little later (Copenhagen, 1961) the USA also published an extraction scheme for separating fragments. They showed the possibility of the isolation by on extraction of alkaline-earth elements.

The data published on regularities of extraction distribution of elements allow the possibility of creating combined - extraction technological scheme for separating all fragment elements radiochemically and chemically pure to be supposed.

The present report deals with the fundamental questions of extraction isolation of long - lived $Sr-90$, $Ce-144$, $Pm-147$, $Eu-155$.

1. Fundamental Regularities of Extraction Isolation of Some Fragment Elements.

The above mentioned four principal long-lived radioactive isotopes: strontium, cerium, promethium and europium represent

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two groups of elements: alkaline - earths and rare - earths; Taking into account that cerium and europium may be changed into the oxidation and reduction state respectively all the extraction processes considered later can be divided into four groups.

1. Extraction of tetravalent cerium
2. Extraction of trivalent rare-earth elements (REE)
3. Extraction of bivalent europium
4. Extraction separation of alkaline-earth elements to produce strontium

A. Extraction Isolation of Cerium - 144.

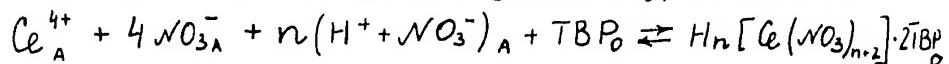
The extraction method of cerium isolation, like all the other known methods of its isolation, is associated with the preliminary changing of cerium into the tetravalent state. Oxidants, such as $KBrO_3$, $KMnO_4$, $KClO_3$, $NaBiO_3$, ozone, as well as electrolytic method of oxidation may be used to oxidize cerium. In contrast to trivalent rare-earth elements, tetravalent cerium is extracted by a great number of oxygen - containing organic solvents having high distribution coefficients, and therefore, can easily be separated from other rare-earths.

At present, tribytilphosphate and di - (2 - ethylhexyl) orthophosphoric acid are mostly used for cerium extraction isolation.

1. Fundamental Regularities of Extraction Distribution of Cerium (IV) and Impurities Accompanying

a) Cerium extraction by TBP.

The reaction of cerium (IV) recovery by TBP from nitrate solutions may be represented, in a general way, as follows:



where $n \leq 2$ in accordance with the cerium coordination number equal to 6. From this equation one can see that depending on the nitric acid concentration in aqueous phase cerium (IV) may be extracted either in the nitrate form or, at higher acidity, in the form of complex acids.

The distribution coefficients for tracer amounts of cerium (IV) are shown in Fig.1.

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When the initial concentration of cerium (IV) in aqueous phase is increased to 5-10 g/l it is extracted by TBP practically completely (D_{Ce} (IV) 350) over a very wide range of nitric acid concentrations.

Both by the method of saturating TBP with cerium nitrate solution and by physical and chemical methods cerium (IV) has been found to pass into the organic phase as a dibasic complex acid with two TBP molecules as distinct from trivalent rare-earth elements being extracted with three TBP molecules. Utilizing this phenomenon one can considerably simplify the process of cerium (IV) extraction by diluted TBP since in this case cerium distribution coefficients decrease according to the quadratic law as cerium (IV) concentration decreases

while those of trivalent REE decrease in accordance with the cubic law. To dilute TBP diluents are used, such as carbon tetrachloride, toluene, xylene, various kerosene fractions, etc. However, when using kerosene as a diluent at high cerium concentrations the organic phase divides into two phases of different composition. In the case of employing other diluents no such complications arise.

As cerium is extracted by TBP by some orders higher than trivalent rare-earth elements under the same conditions, it displaces from the organic phase. Thus, for example, europium distribution coefficients in 4 M HNO_3 decrease from 0.50 to 0.03 when the organic phase is saturated with cerium (IV). Therefore, to increase the degree of purification at isolating cerium (IV) by the undiluted TBP cerium concentrated solutions (250 - 300 g/l) should be used. The above relates only to isolation of large quantities of stable cerium.

Experimental data make it possible to conclude that it is most reasonable to carry out cerium isolation at nitric acid concentration equal to 4 - 5 M/l; by TBP, preliminary distilled or, at least, treated by some oxidant.

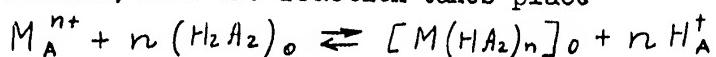
On extracting cerium by 100% TBP from 4 M nitric acid, in the process of a single extraction, the ratio of volumes of organic and aqueous phases λ being equal to 0.2, 98% of cerium pass into the organic phase, while only 10% of rare-earths

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accompanying cerium pass into that phase. Therefore, additional washing of the extract is required to purify cerium. On using diluted, e.g. 50% TBP, notwithstanding, the cerium yield up to 90%, only 1% of concomitant rare-earths contaminating cerium pass into the organic phase, i.e. in this case the conditioned product is obtained as a result of a single extraction:

b) Cerium (IV) Extraction by di - (2 - ethylhexyl) - orthophosphoric Acid

Cerium (IV) extraction by proceeds mainly at the expense of cationic exchange between a cerium ion and acidic hydrogen of the extractant, i.e. the reaction takes place



where H_2A_2 is the extractant dimer molecule.

This extraction mechanism is valid at low nitric acid concentrations in aqueous phase. When extracting from highly acid solutions the passing of the compound being extracted into the organic phase is brought about by means of its solvation by extractant molecules at the expense of phosphorylic oxygen. In accordance with the extraction mechanisms shown cerium (IV) distribution coefficients decrease as the nitric acid concentration in aqueous phase increases; while the rise of distribution coefficients is to be observed over the range of high acidity.

To oxidize cerium, ozone, $KMnO_4$, $KBrO_3$ were used. Cerium oxidation by potassium bromate and ozone was performed in 7-8 M nitric acid as in more dilute solutions cerium oxidizes incompletely due to the decrease of the oxidizing potential of potassium bromate and ozone.

Employing potassium permanganate as an oxidant is complicated by the fact that during cerium oxidation manganese (IV) may form which, being readily extracted is able to contaminate cerium in organic phase. To free cerium from manganese the organic phase is washed by the citric acid solution, which reduce manganese to the divalent state. To reduce manganese (IV) oxalic acid may also be used.

In contrast to tetravalent cerium trivalent rare-earth

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(fig. 2)
elements are extracted by HDEHP with very low distribution coefficients over the entire range of nitric acid concentrations except for the region of low acidity.

Hence, it is most advisable to extract cerium at the nitric acid concentration in aqueous phase equal to 2 M or higher since over this range of acidity the distribution coefficients of rare-earths are very low, while those of cerium (IV) are high.

As cerium (IV) concentration in organic phase is increased trivalent rare-earth elements are displaced since their distribution coefficients decrease at the increase of cerium concentration in organic phase.

To separate cerium (IV) one may use both HDEHP containing no impurities and HDEHP containing HMDEHP and HDEHPP. In the latter case the distribution coefficients have higher values. Since the above impurities, present in the extractant, are first of all associated with cerium the distribution coefficients of trivalent rare-earth elements are practically not affected by them.

B. Extraction of Trivalent Rare-Earth Elements.

Rare-earth fission products constitute 56% of all fragment elements. Separation of rare-earth elements, with the aim of the extraction of chemically and radiochemically pure $Pm - 147$ and $Gd - 155$, is a difficult problem because of the similarity of their chemical properties. All methods of separation of rare-earth elements as well as extraction methods are based on the difference in stability of complex compounds of rare-earth elements, their hydrates or solvates.

The maximum difference in stability constants of various compounds of two neighbouring rare-earth elements equals, on the average, to 2-3, which corresponds also to the difference of 2 - 3 times in the distribution coefficients.

Under specific conditions, this value may be somewhat increased but not more than two times, by performing the separation in the two-phase system, if the order of increasing the distribution coefficients is reversed, which, for example, is observed in the inversion range of distribution coefficient value at the extraction by TBP. The strength of the bond of

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rare-earth elements with the extractant increases from lanthanum to lutecium. The strength of hydrates of rare-earth elements also increases in the same order. At the extraction by TBP, the two phenomena compete with each other; by virtue of this fact, the order of the change of the values of distribution coefficients will correspond to the prevailing process. The inversion phenomenon is of general character. It has been observed on extracting by organic compounds of many classes: by neutral organo-phosphor compounds, carboxylic acids, etc.. On extracting by solvents the bond strength of their solvates with rare-earth elements increases the inversion range with respect the acid concentration, salting out agent, etc..) diminishes.

Of several hundred extractants, tested by us, for separating and concentrating of rare-earth elements neutral and acid organo-phosphor compounds find the widest application, among them commercially prouduced: TBP, Di - isoamyl methyl phosphonate, di-2 (ethylhexyl) orthophosphoric acid, as well as aliphatic carboxylic acids (fraction C₇ - C₉) are very cheap.

I. General Regularities of the Distribution of Rare-Earth Element at Extracting by Organo-Phosphor Compounds

a) Neutral Extractants. The presence of grouping p = 0 is characteristic of all these extractants. Extraction proceeds at the expense of the formation of bonds between phosphoryl oxygen and metal or hydrogen of complex acid of rare-earth elements.

At low and moderate acidity compounds $M(NO_3)_3 \cdot 3S$ are extracted (S - an extractant molecule); at high acidity rare-earth elements in organic phase are present as complex acids, of a limiting composition $H_3M(NO_3)_6 \cdot 3S$

At the extraction by TBP the highest distribution coefficients are 1.8 - 2 for highly acidic solutions. Although TBP is characterized by smaller distribution coefficients than, for example, dialkylphosphoric acids, it has the advantage over them in that the distribution coefficients of fragment rare-earth elements (i.e. elements of cerium group) depend little on their

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concentration over a wide range. It is very important since after concentration, which, as a rule, precedes separation, the concentration of rare-earth elements may amount to 40 - 50 g/l

Similar results are obtained at the extraction by D_4AMP for which there are somewhat higher distribution coefficients and somewhat lower distribution factors (Fig.5).

The following systems may be proposed for concentrating fragment rare-earths elements: TBP or D_4MP , a salting out agent in weak-acid solution, phosphin oxide is a slightly acid solution of rare-earth elements.

b) Acid Organo-Phosphor Compounds (dialkylphosphoric acids)

The maximum difference in distribution coefficients of rare-earth elements amounts to 2.5 - 2.7.

Monoalkylphosphoric acids give much higher values of distribution coefficients, the distribution factors of lower cerium elements, however are immeasurably lower at the extraction by these compounds.

Organic-phosphor acids may be recommended to separate tracer amounts of rare-earth elements and to concentrate them.

c) Application of Complexing Agents

Under the conditions where inversion occurs or rare-earth elements are extracted practically with no separation, to secure maximum selectivity such complexing agents may be introduced into the extraction system which both themselves and their compounds with rare-earth elements are soluble only in aqueous solution.

In our work we selected such complexing agents which ensure the maximum difference in stability constants of compounds with rare-earth elements.

Under the conditions of inversion the heavier rare-earth elements are extracted worse than the lighter ones; the former in aqueous phase making complexes more readily. As a result of imposing these phenomena the maximum difference in the behaviour of rare-earth elements is attained. Lesser difference is observed at extraction under the conditions where rare-earth elements in the absence of any complexing agent, are extracted practical-

ly without separation (Fig.4).

Thus, for example, the extraction of rare-earth elements in the system: nitrylotriacetic acid - carboxylic acid (poorly selective extractant), resulted in the following distribution factors for each pair: $\text{La}/\text{Ce} = 6$; $\text{Ce}/\text{Pr} = 3$; $\text{Nd}/\text{Pr} = 2.2$.

In practice to effect the extraction process of separating fragment rare-earth elements these processes should be reduced to two limiting cases; the calculation as well as bringing about an extraction process on multiple-stage installations being considerably simpler.

In the former case, for example, at the TBP extraction the distribution coefficients of rare-earth fragments ($\text{Nd}, \text{Pr}, \text{Lu}^{(III)}$) are little changed at increasing their concentration up to 50-100 g/l; their distribution proceeds independently.

In the latter case, for example, when using acid extractants or introducing complexing reagents, one should work at the complete saturation of one of the phases. Then the process of extraction separation is based on the mutual displacing of elements, more or less constant values of separation being retained.

C. Extraction Separation of Divalent Europium

Almost all methods of europium separation are based on its reduction to divalent state or to a metal. In the former case europium is precipitated or co-precipitated as sulphate, in the latter case the separation is carried out by the formation of an amalgam. Recently, the europium separation is effected by extracting, also after preliminary europium reduction to the divalent state. The europium reduction to the divalent state was effected by zinc dust, amalgamated zinc or at the mercury cathode.

As the europium oxidation-reduction potential +3/+2 has a low value (0.43V) it is readily oxidized by atmospheric oxygen. Therefore during carrying out the process of europium separation one should create inert atmosphere or take other precautions as well.

The extraction separation of trivalent rare-earth elements was brought about either by means of acid extractants (e.g., by Di-2 (ethylhexyl) phosphoric acid in chloride medium) or by neut-

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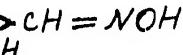
ral alkylphosphoric extractants (e.g., by phosphonates or triphosphoxides in nitrate medium).

D. Strontium Separation

At present extraction methods of separation are applicable practically to all metals of the Periodic System, the greatest difficulties being encountered for alkaline-earth and alkaline groups of metals. The most serious work on separating alkaline - earth elements aiming at obtaining pure strontium - 90 was reported in Copenhagen in 1960.

We tested a great number of various complexing agents and extractants for the separation of alkaline-earth elements. The most suitable system, in our opinion, has turned out to be the solution of salicylaldoxime in TBP ammonia - aqueous solution of alkaline-earth elements.

Salicylaldoxime (SAO) possesses the same active groupings



like oxyquinoline derivatives.

The distribution coefficients of salicylaldoxime itself are changed negligibly at the ρH change from 0 to 12 and have the value far greater than 80.

The distribution coefficients of alkaline-earth elements have rather high values only when organic compounds, such as TBP, DAMP, and the like, are used as diluents.

Equilibrium is reached within several minutes; the reaction of forming the complex being extracted is reversible.

When changing the concentration of a complexing agent the distribution coefficients of Ca, Sr, Ba are practically changed proportionally to the concentration change of SAO, which indirectly points out to the salicylaldoxime dimerization in organic phase. In Figs 5 and 6, are shown data on the dependence of distribution coefficients of alkaline-earth elements upon the concentration of alkali, ammonia and alkaline-earth metals themselves. The values of the distribution coefficient for calcium-strontium and strontium-barium pairs, the ammonia concentration being 0.1N - 2N NH_4OH , are, on the average, 80-100 and 2-3 respectively. At the above value of the distribution coefficient, the process of separating calcium from

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strontium is not very difficult and may be effected either as a periodic process or at the countercurrent extraction installation at the minimum number of stages.

2. Extraction Installations

Practical bringing about of extraction processes of radioactive isotope separation may be accomplished by various methods. In case of europium, strontium and cerium separation the extraction process is quite easily effected periodically. When separating trivalent rare-earth elements, with the aim of obtaining a concentrate of soft beta, gamma-radiators ($Eu-155, Pm-147$) one should use multiple-stage extraction installations adapted for distance control.

To separate rare-earth elements extractors mainly of two types, i.e. countercurrent and semicountercurrent, are used.

Both types of extractors used by us are mixer-settlers. As the extraction installations are intended for distance operation mixing up has turned out to be effected more conveniently by the air blowing or vibration method.

In both cases the suction of phases is carried out simultaneously with the mixing up.

The description and schemes of two extraction installations of countercurrent and semicountercurrent types with air blowing are given later. Both installations are adapted for distance operation and for the maximum volume reduction the cells are of tubular construction. Both installations are assembled of standard interchangeable sections.

The cell construction employed by us has the following features: to raise specific efficiency the sediment zone has the form of a horizontal tube changing to the vertical separator the separator ensures the partition of both streams and has a water seal at the verflow of the heavy phase securing the stable position of the interface of phases over the given range of the change of specific weights.

The scheme of one cell is shown in Fig. 7. The effeciency of the installation is rated at 20-30 litres per hour according to the sum of the streams and allows the change of the stream ratio from 1/10 to 10/1. Air consumption is about 150 e/h per cell. To stabilize air consumption and the operation of the

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whole installation, on each cell throttle washers are placed having a special device to prevent their soiling. The cell efficiency is close to 100%. The total number of cells is equal to 30, which fully ensures the production of pure promethium.

Semicountercurrent extractor consists of separate cells; one phase in each cell is stationary, the other passes successively through all the cells, effecting the separation of the mixture of components preliminary introduced into a few first cells. The semicountercurrent installation of 50 cells is also intended for distance control. The scheme of the construction of one cell is shown in Fig.8. The sedimentation chamber of the cell (5) is made in the form of a flat disk with the spiral passage of emulsion. The emulsion circulation through settlers as well as along the inner contours is brought about from one complex aerolift. The cell ensures the stable operation at efficiency (according to the eight phase) equal to 7 working volumes of the cell and at the phase ratio in emulsion equal to 1/10. Special safety devices are provided in the cells, these secure an automatic switching off of any cell that stopped operating.

3. Technological Process of Separation of Long-Lived Fragment Elements

The initial solution to be separated is a nitrate concentrate of fragment elements containing corrosion products and impurities introduced into the solution from reagents.

The first operation, the concentration of strontium and rare-earth elements is performed most reliably by means of oxalate coprecipitation of rare-earth and alkaline-earth elements.

Obtained in this way the nitrate solution of rare-earth elements and strontium after the destruction of oxalic acid, practically contains no iron, chromium and a number of other radioactive and stable impurities.

The total content of rare-earth elements in the final solution reaches 5-10 g/l while the solution radioactivity depends on the ageing of the product taken for processing.

Strontium - 90, cerium - 144, promethium-147 and euro-

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pium-155, individually, are most reliably and simply separated by extraction methods.

The first stage is the separation of radioactive cerium. The separation is carried out in two ways: (a) cerium is oxidized in 7-8 N HNO_3 , by ozone or bromate and extracted by 0.5 N $HDEHP$ solution or 50% TBP; (b) the sum of rare-earths is extracted by $HDEHP$ out of the weak-acid or buffer solution, then the organic phase is washed by the oxidant solution in nitric acid, pure cerium remaining in organic phase and trivalent rare-earth elements with no cerium remaining in aqueous phase. When the ratios of the volumes of initial solution, extractant and washing solutions have been chosen properly it is rather easy to effect practically pure separation of the initial concentrate of the radioisotopes into three fractions pure radioactive cerium-144, the strontium-90 concentrate and promethium concentrate of rare-earth elements with no cerium.

In all cases pure strontium-90 was obtained after cerium isolation and separation of rare-earth elements. The main impurities from which strontium should be separated are calcium, which may be 20-30 times the weight of strontium, and also barium and lead.

Calcium disposal is produced by the extraction with 1-2 M calicetylaldoxime solution in tributylphosphate from about 1 M ammonia solution of alkaline rare-earths. For example 99% of Ca are extracted and > 85% of strontium are left even by simple periodic extraction successively by three equal volumes of 2 M solution of SAO and TBP from aqueous solution of 1 M calculating on NH_4NO_3 and $NaNO_3$ and containing 0.4 M $Ca(NO_3)_2$ and 0.005 M $Sr(NO_3)_2$.

Pure promethium-147 is produced in an ordinary way, by TBP extraction either on the countercurrent installation only or by combination of countercurrent and semicountercurrent processes.

The radioactive europium separation is most easily effected also by extraction after its preliminary reduction with zinc dust or with amalgamated zinc in chloride medium.

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Conclusions

1. In this report are presented the results of studying the main regularities of the extraction isolation of a number of long lived fragment elements.
2. The investigation of cerium extraction and micro- and macrocomponents in solution has shown the possibility of practically complete cerium separation from oxidized solution by a) TBP both diluted and undiluted b) H_2EHP from 2 M solution on the nitric acid. The presence of $M - 2 - EHPA$ and $D - 2 - EHPPA$ has not been shown to affect the course of the process.
3. The perspective of employing a number of extractants for separating trivalent rare-earth elements have been shown. The best results have been obtained for tributylphosphate diisoamyl methyl phosphonate, $HDEHP$ and for carboxylic acids (fraction $C_7 - C_9$) as well.
4. The advisability of using complexing agents in the systems where inversion occurs has been shown.
5. To extract europium it has been recommended to reduce it to the di-valent state with the subsequent extraction separation.
6. The distribution of alkaline earth elements has been studied in the system: the salicylaldoxime solution in TBP - aqueous ammonia solution of alkaline earth elements.
7. The perspectivity of using SAO to separate and produce radio- and chemically-pure strontium-90 has been shown.
8. The extraction installation operating on the principle of semicountercurrent and countercurrent, used in the course of work, has been described.
9. All-extraction scheme for extracting principal long-lived fragment elements has been recommended.

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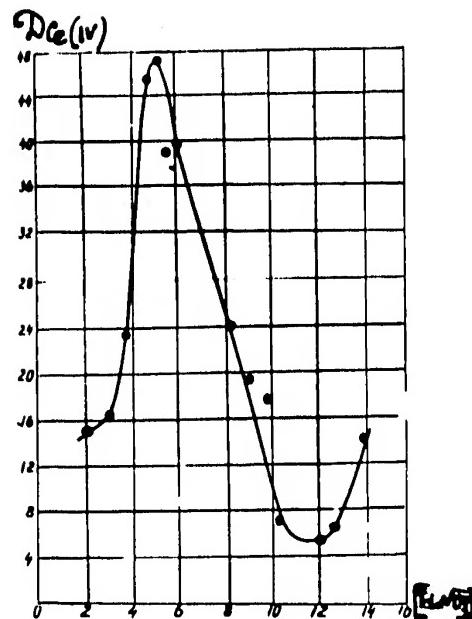


Fig. 1.

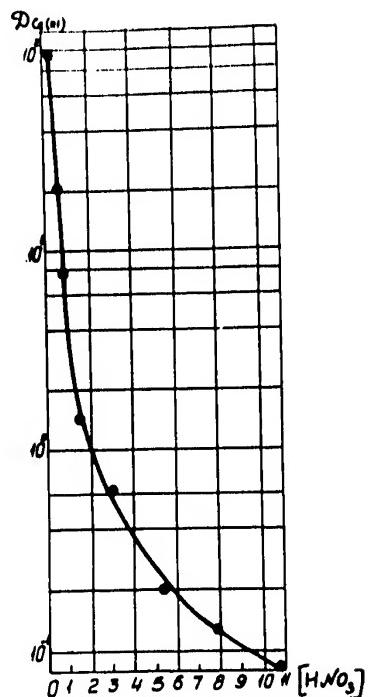


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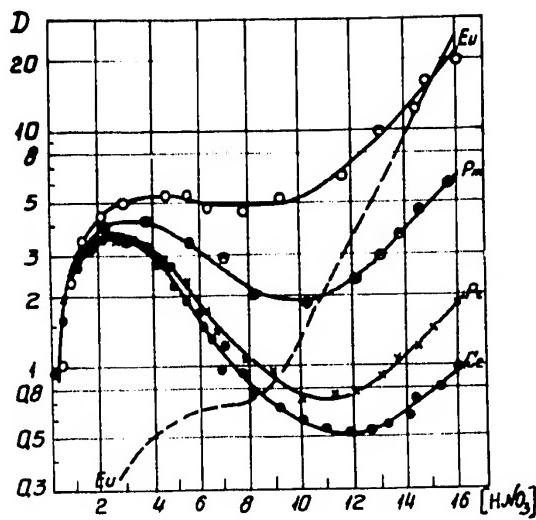


Fig. 3.

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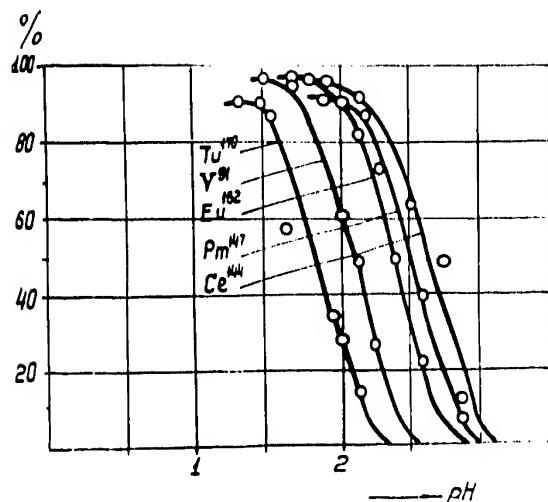


Fig. 4.

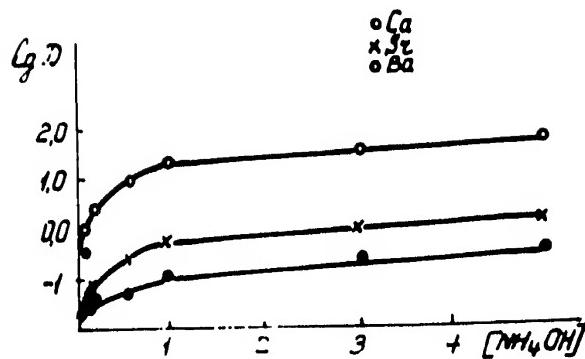


Fig. 5.

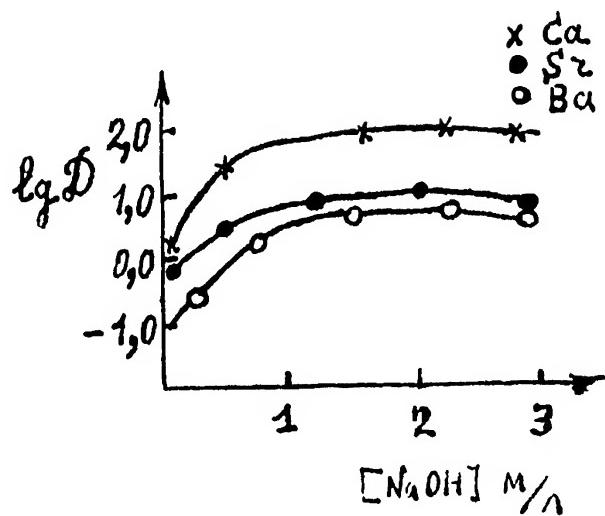


Fig. 6.

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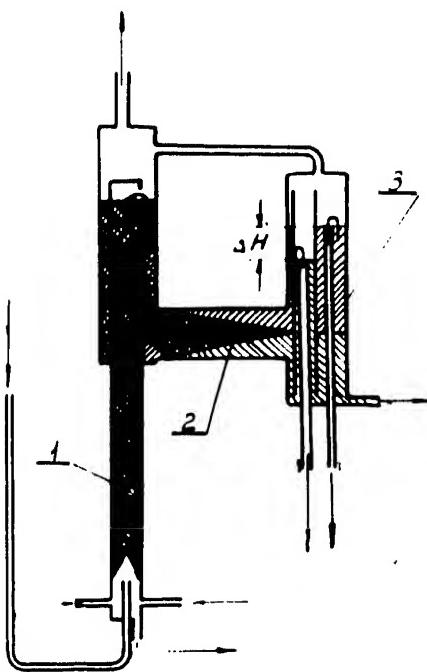
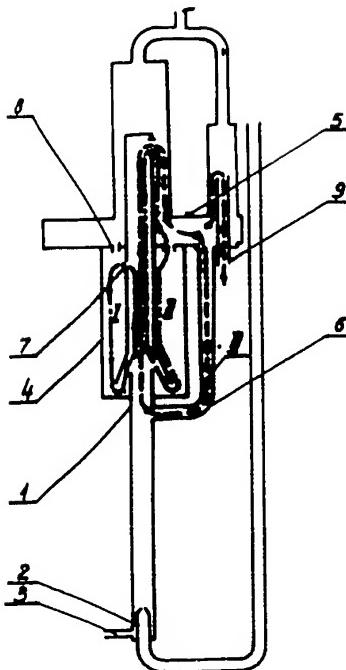


Fig. 7.



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Fig. 8.

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Subscripts to Pictures

- Fig. 1. Cerium (IV) distribution between nitric acid and TBP.
- Fig. 2. Cerium (IV) distribution between nitric acid and 0.33 M HDEHP solution.
- Fig. 3. The dependence of distribution coefficients of tracer quantities of europium, promethium, praseodymium and cerium on nitric acid concentration at the extraction by DiAMP
- Fig. 4. The distribution of tracer amounts of rare-earth elements between TBP and 6 N NH_4OH in the presence of the excess of ethylenediaminetetraacetic acid depending on the pH of aqueous phase.
- Fig. 5. The dependence of Ca , Sr , Ba distribution coefficients on the NH_4OH concentration at the extraction by 1 M SAO in TBP.
- Fig. 6. The dependence of Ca , Sr , Ba distribution coefficients on $NaOH$ concentration at the extraction by 1 M SAO in TBP.
- Fig. 7. The scheme of the countercurrent extraction cell with air stirring.
- Fig. 8. The scheme of the semicountercurrent extraction cell with air stirring.